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Renewable Hydrocarbon Diesel Fuel Properties and Performance Review (CRC Report No. DP-08-18)

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Renewable Hydrocarbon Diesel Fuel Properties and Performance Review

CRC Project No. DP-08-18

September 2018

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Performance Committee

Diesel Performance Group

Biodiesel and Renewable Diesel Panel

Table of Contents

Acronyms and Abbreviations

CEN   -   European Committee for Standardization

CFI   -   cold flow improver

CFPP   -   cold filter plugging point

CGSB   -   Canadian General Standards Board

CN   -   Cetane number

CP   -   cloud point

CRC   -   Coordinating Research Council

CTO   -   crude tall oil

EISA   -   Energy Independence and Security Act of 2007

EPA   -   United States Environmental Protection Agency

EPAct   -   Energy Policy Act of 1992

FAME   -   fatty acid methyl esters

FT   -   Fischer-Tropsch

GTL   -   gas-to-liquids

HBD   -   hydrogenated biodiesel

HDRD   -   hydrogenation -derived renewable diesel

HEFA   -   hydrogenated esters and fatty acids

HFRR   -   high frequency reciprocating rig

HVO   -   hydrogenated vegetable oil

LTFT   -   low-temperature flow test

LTO   -   low temperature operability

RD   -   renewable hydrocarbon diesel

ULSD   -   ultra-low sulfur diesel

1. Introduction

Compression ignition engines, commonly referred to as diesel engines, are critical for goods transportation and industry on land and sea. Significant changes have been required of diesel fuel composition over the past several decades. In the United States, the Environmental Protection Agency (EPA) lowered on-highway diesel sulfur content to 0.05 wt% (500 ppm) in 1993. This is known as low-sulfur diesel. In 2006 sulfur content of diesel fuel was lowered further to 15 ppm and is known as ultra-low-sulfur diesel (ULSD).

Laws such as the Energy Policy Act (EPAct) of 1992 and the Energy Independence and Security Act (EISA) of 2007 began to mandate the use of alternative fuels. Examples of alternative diesel fuel formulations include gas-to-liquid diesel (GTL, also known as Fischer-Tropsch (FT) diesel), biodiesel, and renewable hydrocarbon diesel (RD). Congress adopted the term biomass-based diesel in EISA to include biodiesel and RD. The term "biodiesel" is reserved for a diesel fuel blend component that is produced from vegetable oils, animal fats, or waste cooking oil by an esterification process and consisting of fatty acid methyl esters (FAME). Renewable diesel is commercially produced currently by hydrotreating biomass-derived materials such as vegetable oils, waste cooking oils, animal fats, and crude tall oil (a residue of the wood pulping process). World production of RD approached 1.2 billion gallons in 2014.[1] Hydrotreating is a process in which hydrogen is used to remove oxygen and double bonds creating primarily long chain hydrocarbons along with other molecular structures that are like those in conventional petroleum diesel. Commercial processes also employ an isomerization step to create branched alkanes that improve low temperature properties to acceptable levels.

The purpose of this document is to describe the properties of RD in neat (100%) form and in blends with conventional petroleum diesel, as well as to describe handling and blending practices. This document is intended to provide a guide for the end user, fuel producer/distributor, and vehicle/equipment manufacturer.

For purposes of this report, RD is defined as a hydrocarbon oil derived from hydrotreating fats, vegetable oils, used cooking oil, or crude tall oil that, with the addition of chemicals to enhance performance if required. The resulting fuel should conform to the requirements of a commercial standard for fuels to be used in compression ignition engines; or can be a blendstock for such fuels.

Renewable hydrocarbon diesel is also called hydrogenated vegetable oil (HVO), hydrogenation-derived renewable diesel (HDRD), hydrogenated esters and fatty acids (HEFA), or (inaccurately) hydrogenated biodiesel (HBD) and is frequently referred to as simply renewable diesel (RD).

The GTL process also produces a hydrocarbon diesel that can be termed renewable if produced from gasification of a renewable resource such as biomass or municipal solid waste. The properties and performance of GTL diesel are well known and have been described in several previous publications.[2,3] They are not covered in this guide. While other processes can also produce biomass-based hydrocarbons that are suitable for use in diesel fuel, these are not produced at commercial scale in 2018. They also are not covered in this guide.

Unconverted vegetable oil or waste cooking oil has also been considered as a diesel fuel blend component and is sometimes referred to as viscous renewable diesel. The high viscosity, high cloud point (CP), and high boiling point of this material makes it unsuitable for use in conventional diesel engines because it may cause injector and combustion chamber deposits, and may accumulate in engine lubricant.[4,5] A statement from the Truck and Engine Manufacturers Association recommends avoiding this material in diesel fuel.[6] Therefore this material is not discussed further in this guide.

2. Production Processes

Many different processes exist for manufacturing hydrocarbon biomass-based diesel fuels:

1. Catalytic hydrotreating of triglycerides and fatty acids, or of crude tall oil
2. Co-Processing with petroleum
3. Biomass-to-Liquids (FT diesel)
4. Biogas-to-Liquids (GTL/FT diesel)
5. Catalytic Upgrade of Sugar
6. Fermentation of Sugar
7. Biomass fast pyrolysis /hydrotreating

This guide describes the properties of renewable diesel produced by catalytic hydrotreating of triglycerides and fatty acids, or hydrotreating of crude tall oil (CTO). Both processes are practiced at commercial scale. The remaining processes are predominantly in the research and development stage. A brief overview of these processes is provided in Appendix I.

2.1 Renewable Diesel from Triglyceride and Fatty Acid Feedstocks

RD produced from these feedstocks also is referred to as hydrogenated esters and fatty acids (HEFA). While there are many different production processes being practiced, all are believed to consist of the same primary steps: pretreatment, hydrogenation/deoxygenation, water removal, hydroisomerization, and product separation.[7,8] A simple process schematic is shown in Figure 2.1. Pretreatment is to remove impurities that may poison the catalysts used in subsequent steps. The hydrogenation/deoxygenation step hydrogenates double bonds and removes oxygen by hydrogenation (producing water), decarbonylation (producing CO), or decarboxylation (producing CO_2).[9,10] To the extent that oxygen is removed by decarbonylation or decarboxylation hydrogen consumption is reduced, however, this comes at the expense of losing some of the carbon in the feedstock to CO_2 rather than it being incorporated into the product (carbon yield loss).

The hydrocarbon product from hydrogenation/deoxygenation consists of long chain alkanes that, while having a very high cetane number (CN), also exhibit a CP of over 20°C.[11] To improve the low temperature performance of the fuel and to lower the CP, this material is hydroisomerized after removal of the water and product gases. Hydrogen pressure is on the order of 1 to 2 MPa. Hydroisomerization is acid-catalyzed formation of isoparaffins with some cracking to lower molecular weight products.[12,13,14] The operating parameters of the hydroisomerization reactor can be varied to tailor the CP seasonally and to produce differing yields of diesel, jet, naphtha, and light gases. Generally lower CP – which requires more aggressive hydroisomerization – also causes more cracking.
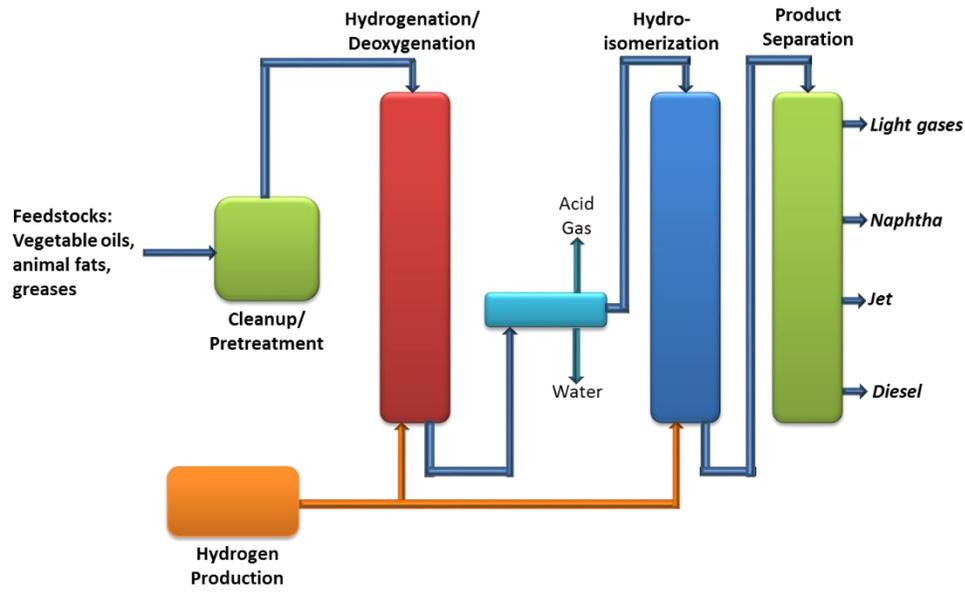
Figure 2.1. Basic process steps in RD production from fats and oils.

2.2   Renewable Diesel from Crude Tall Oil Feedstock

Crude tall oil is significantly different from the fats and oils feedstocks used to make biodiesel and the renewable diesel described in the previous section, yet the process steps for making renewable diesel are similar.[15] CTO is a byproduct of the Kraft pulping process that converts wood into wood pulp for making paper.[16] This is an alkaline process where fatty and rosin acids in the wood are saponified. This soapy material, and neutral lipid compounds such as sterols that are soluble in the soapy material, is acidulated to yield free rosin and fatty acids and the neutral compounds which make up CTO. It is a dark brown product resembling tar with an unpleasant odor. The composition depends on the type of wood being processed but falls in the following ranges:

- Fatty acids: 40 to 50 wt%
- Rosin acids: 30 to 50 wt%
- Neutral compounds: 10 to 30 wt%

The fatty acids are similar to those in fats and vegetable oil feedstocks used to make biodiesel and renewable diesel. The rosin acids, however, are very different. The 20 carbon abietic acid (Figure 2.2) is the primary constituent along with a group of similar acids. The neutral components are predominantly esters, sterols and hydrocarbons, with β-sitosterol (Figure 2.2) being a typical neutral component.[17] Ring opening and cracking reactions are required to convert these types of molecular structures to diesel-like components.

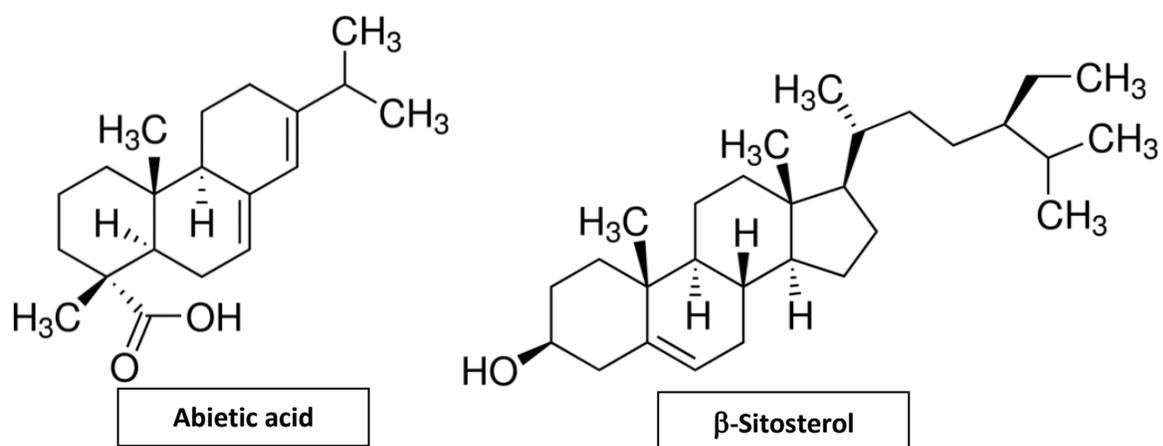**Figure 2.2. Representative components of CTO rosin acids (left) and neutral fraction (right).**

The RD production process from CTO involves an initial pretreatment/cleanup step to remove solid particles and metals.[15,17, 18] UPM,[i] for example, describes a single step hydrotreating followed by fractionation to product diesel and other products.[15,17]

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[i] United Paper Mills - Finnish Forest Industry Company

3. Renewable Hydrocarbon Diesel Properties

Conventional diesel fuel is not a single molecule but a mixture of paraffins, naphthenes (cycloparaffins) and aromatics (olefins may be present at low concentration). The property requirements for diesel fuels are specified by various standard setting organizations such as ASTM International, Canadian General Standards Board (CGSB) or the European Committee for Standardization (CEN). These standards define the minimum acceptable properties of fuels for use in diesel engines and are frequently cited in product transfer contracts and other aspects of commerce.

3.1 Diesel Fuel Standards

The requirements of the ASTM, CGSB, and CEN standards for diesel fuel oils are shown in Table 3.1. Specific low temperature operability requirements are also a part of EN590[19] but are not included here. None of the three diesel fuel standards specifically limit the content of RD. Also shown in Table 1 are the requirements of EN15940: Automotive fuels - Paraffinic diesel fuel from synthesis or hydrotreatment - Requirements and test methods.[20] Most of the specifications listed in EN 15940 meet the corresponding specifications required in the three conventional diesel fuel specifications. The exceptions include lower density at 15 °C than allowed by EN590; and higher carbon residue and kinematic viscosity at 40 °C than allowed ASTM D975 or CGSB 3.517. The paraffinic diesel specification defines a lower density range when compared to EN 590. EN 15940 has similar specification for carbon residue as EN 590 but is more stringent than ASTM D975[21] and less stringent than CGSB 3.517.[22] The viscosity minimum and maximum mirror those of EN 590 but are slightly higher than limits in ASTM D975 and CGSB 3.517. EN 15940 limits aromatics to less than 1.1 wt% for RD compared to 35 vol% for D975 diesel. EN 15940 limits for sulfur are lower than EN590, D975, and CGSB 3.517.

Table 3.1. Diesel Fuel Specifications: Corresponding test methods and footnotes are found in Appendix II.

Property	EN 590:2013+A1:2017		ASTM D975-17a		CAN/CGSB 3.517:2017		EN 15940:2016/A1:2018	
	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
Cetane Number	51	--	40	--	40	--	70/ 51[ǂ]	--
Cetane Index	46	--	40[a]	--				
Density at 15°C	820 kg/m^3	845 kg/m^3	--	--	--	--	765 kg/m^3 780 kg/m^{3ǂ}	800 kg/m^3 810 kg/m^{3ǂ}
Polycyclic Aromatic Hydrocarbons[b]	--	8 % (m/m)	--	--	--	--	--	--
Aromaticity	--	--	--	35% (v/v)[a]	--	--	--	1.1 % (m/m)
Sulfur Content	--	10 mg/kg	--	15 mg/kg	--	15 mg/kg	--	5 mg/kg
Manganese Content	--	2 mg/L	--	--	--	--	--	--
Flash Point	55°C	--	52°C/38°C †	--	40°C	--	55°C	--
Carbon Residue (on 10 % distillation residue)	--	0.3 % (m/m)	--	0.35 % (m/m)	--	0.2 % (m/m)	--	0.3 % (m/m)
Ash Content	--	0.01 % (m/m)	--	0.01 % (m/m)	--	0.01 % (m/m)	--	0.01 % (m/m)
Water Content	--	200 mg/kg	--	--	--	--	--	200 mg/kg
Total Contamination	--	24 mg/kg	--	--	--	--	--	24 mg/kg
Water and Sediment			--	0.05 % (v/v)	--	0.02 % (v/v)	--	0.02 % (v/v)
Copper Strip Corrosion Rating	Class 1 rating		--	No. 3	--	No. 1	Class 1 rating	
Fatty Acid Methyl Ester (FAME)	--	7 % (V/V)	--	5% (V/V)	--	--	--	7 % (V/V)
Oxidation Stability	20 h	25 g/m^3	--	--	--	--	20 h	25 g/m^3
Lubricity, Wear Scar Diameter at 60 °C	--	460 μm	--	520 μm	--	460 μm	--	460 μm
Viscosity at 40 °C	2 mm^2/s	4.5 mm^2/s	1.9 mm^2/s 1.3 mm^2/s†	4.1 mm^2/s 2.4 mm^2/s†	1.7 mm^2/s	4.1 mm^2/s	2 mm^2/s	4.5 mm^2/s
Distillation % (V/V) Recovered at 250 °C % (V/V) Recovered at 350 °C 95% (V/V) Recovered at:	--% (V/V) 85% (V/V) --°C	<65% (V/V) -- % (V/V) 360°C	--	--			--% (V/V) 85% (V/V) --°C	<65% (V/V) --% (V/V) 360°C
Distillation Temperature, 90% Recovered	--	--	282°C --°C	338°C 288°C †	--	360°C	--	--
Conductivity[d]	--	--	25 pS/m	--	25 pS/m	--	25 pS/m	--
Acid Number	--	--	--	--	--	0.1 mg KOH/g	--	0.1 mg KOH/g

3.2   Neat Hydrocarbon Renewable Diesel Properties

Table 3.2 summarizes literature reports on the properties of HEFA and CTO derived RD fuels in neat form.   The properties are generally within the ranges allowed by the ASTM D975 Grade No. 2-D S15 diesel fuel standard (fuel additives are necessary to meet some requirements). Notable are the very high CN and low density (relative to EN590 requirements) of HEFA -derived RD. While it generally has a higher heating value per mass than conventional diesel fuels, its heating value per gallon is generally slightly lower than that of conventional diesel. For the studies considered in Table 3.2, the average lower heating value for HEFA RD was 34.4 MJ/L, which was on average 4.3% lower than for the petroleum diesel fuels included for comparison in the same studies. Differences as high as 5.5% were reported.[23] Results for CTO-derived RD come from a single reference, but also show high CN. These and other properties not covered in the table are discussed below.

Cetane number

Hydrotreating of vegetable oils, waste cooking oils, animal fats and similar materials produces long chain alkanes with typically 15 to 20 carbon atoms. Given that n-hexadecane (C16) defines 100 on the CN scale, this deoxygenated oil will have a CN over 100. However, the CP of this material may be as high as 20°C, making it impractical to use as a fuel or blendstock. To eliminate this barrier, the long chain alkanes are isomerized to introduce branching, lowering the CP but also lowering the CN. Figure 3.1 shows CN and CP results for a set of RD samples examined by Smagala and coworkers.[11] The high CP/high CN sample on this chart was not isomerized. Note that in the practical range of cloud points (0 to -30°C) there is no correlation between CN and CP. However, all the samples with CP in this range exhibit CN above 70.

Much less has been reported about the molecular structures that make up hydrotreated tall oil RD, however CN has been reported to be 65.[18]
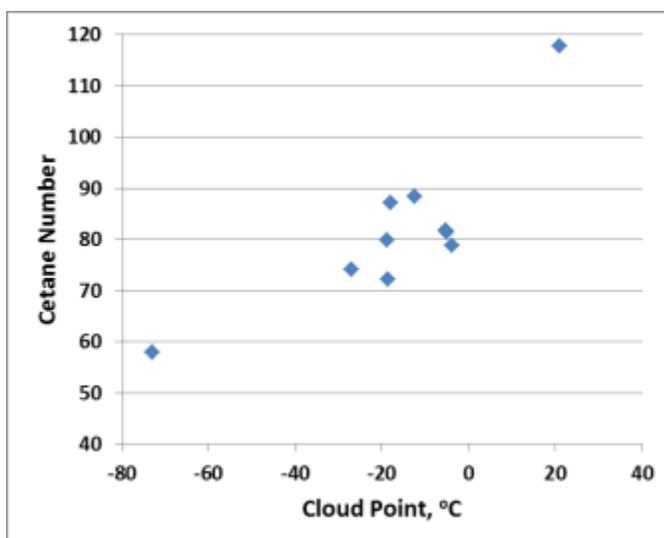

Figure 3.1. Cetane number and cloud point for RD produced by hydrotreating of vegetable oils, waste cooking oils, and animal fats (data from reference 11).

Table 3.2. Key properties of neat HEFA and CTO based renewable diesel taken from literature reports.

Property	Test Method	ASTM D975 Limit (No. 2-D, S15 Grade)	HEFA RD[11,23,24,25,26,27,28,29]	CTO RD[18]
Flash point, °C, min	D93	52	59 to >125	78
Distillation Temperature, °C, 90% volume recovered	D86	282-338	287 to 315	94 v% recovered at 350°C
Kinematic Viscosity, mm2/s at 40°C	D445	1.9-4.1	2.5 to 3.6	3.5
Ash, %m, max	D482	0.01	<0.001	<0.005
Sulfur, ppm, max	D5453	15	<3	<1
Copper Strip Corrosion Rating, max	D130	No. 3	1	1
Cetane Number, min	D613	40	72 to 95	65
Aromaticity, %v, max	D1319	35	0	
Cloud point, °C, max	D2500	Report	-27 to 7	Not reported
Lubricity, HFRR at 60 °C, micron, max	D6079/D7688	520	>700 (additive required)	228[b]
Conductivity, pS/m, min	D2624/D4308	25	Not reported (additive required)	Not reported
Density, kg/m3 at 15°C	No requirement[a]	--	775 to 786	814
Lower Heating Value, MJ/kg	No requirement	--	43.7 to 44.5	Not reported
Lower Heating Value, MJ/L	No requirement	--	34.3 to 34.8	Not reported

[a] EN590 requires density in the 820 to 845 kg/m^3 range, EN15940 requires density to be in the 765 to 810 kg/m^3 range

[b] It is not clear from the cited source if this sample contained lubricity additive

Low-temperature operability

The low temperature operability (LTO) limit of a diesel fuel is the lowest temperature at which the fuel will be able to flow properly and supply the engine for normal operations. Traditional petroleum-based diesel fuel is a complex mixture of paraffinic and aromatic hydrocarbons that can range from C_8 to C_{32},[30] with the bulk of the hydrocarbons between C_{10} to C_{22}.[31] LTO performance of a diesel fuel is determined by several temperature dependent factors including viscosity and solubility of n-paraffins (wax). Viscosity will increase as temperature decreases which can reduce flow to the engine. Precipitated wax is a well-known factor restricting flow to the engine. Solubility of wax in diesel fuel is determined by the total wax content, wax size distribution, and the ratio of non-linear paraffins and aromatic species in the matrix.

RD fuels can pose a challenge for LTO performance. RD fuels that do not undergo isomerization are generally waxes ranging from C_{15} to C_{18}.[11] This narrow composition of n-paraffins makes LTO below the CP very difficult to achieve with cold flow improver (CFI) additives. However, the low-temperature operability properties of both HEFA and CTO-based RD can be altered by processing conditions. Smagala and coworkers report, for example, a HEFA RD sample with a CP of -27°C.[11] Freezing points in the jet fuel range (<-40°C) are also possible using isomerization.[32] There does not appear to be any published information on CTO based RD cold flow properties in neat form. In any case, low-temperature operability requirements are met on the finished fuel, and if the neat RD is to be used as a blendstock there are many different strategies available to meeting these requirements.

Smagala and coworkers reviewed a wide range of paraffinic fuels with varied feed stocks and levels of post-processing. The RD fuels evaluated show a large variation in low temperature properties which can be attributed to the different levels of isomerization.[11] For example, a non-isomerized hydrogenated animal fat derived RD had a CP of +24 °C while an isomerized animal fat had a CP of -19 °C. Isomerization is likely required for RD to meet fit-for-purpose LTO properties of the finished fuel.

LTO of petroleum diesel fuel can be enhanced with the use of CFI additives. CFI additives co-crystalize with the waxes in diesel fuel to alter their size and shape. These modified wax crystals allow adequate fuel to flow through the filter. A more detailed explanation of the function of these additives and relevant test methods can be found in numerous publications including CRC Report 671.[30]

Increasing quantities of wax in diesel fuel will decrease the efficacy of traditional CFI additives. This effect is exacerbated when the waxes are of the same or similar chain lengths,[33,34] as seen in RD fuels. Non-isomerized RD fuels are relatively impossible to treat with traditional CFI technologies due to the nature of their wax content. Using non-isomerized RD fuel as a blendstock would significantly increase the waxes in a narrow range while decreasing the total solubility of the fuel.

Isomerization of RD fuels reduces the level of wax in favor of iso-paraffins. The extent of isomerization is correlated with the improvement in LTO properties. However, the remaining n-paraffins can still limit the effectiveness of CFI additives. Only a small amount of work has been published on the effect of CFI additives on neat RD fuels. To date, this work indicates that typical CFIs have little impact on improving LTO of neat RD.[35]

Lubricity

Lubricity is measured using the high-frequency reciprocating rig (HFRR) test (ASTM D6079, D7688, or ISO 12156-1 test methods) and the result is reported as a wear scar diameter, with higher values indicating poorer fuel lubricity. Diesel fuels with very low heteroatom content such as ULSD, FT-diesel, and RD generally require a lubricity improving additive to meet minimum lubricity requirements. Consistent with this, an HFRR wear scar diameter of 727 µm was reported for an unadditized RD sample,[26] which is well above the allowable wear scar diameter level in any of the diesel fuel specifications. Therefore, lubricity improver additives are commonly used with ultra-low sulfur diesel, FT-diesel, and RD. Lubricity additives are often added just before the product is delivered to the retail level to provide the necessary lubricity while preventing trailback of additive into other products in multiproduct pipelines.

Field experience indicates that for conventional diesel fuel injection systems are protected against excessive wear by the lubricity requirements in the major diesel fuel specifications. There have been indications some Paraffinic Renewable Diesel fuels do not always respond in a similar manner as conventional diesel fuels regarding seizure wear protection. The reader is referred to CEN 15940 Appendix A for information regarding seizure protection.[20]

Conductivity

Meeting the conductivity requirement is important for safe handling during transport and blending, and low conductivity values are frequently observed for diesel fuels with low heteroatom content. While no values of conductivity were reported in the literature, RD producers, like ULSD producers, add antistatic additives early in the distribution system to improve conductivity and ensure safe handling.[36]

Storage and thermal stability

Smagala and coworkers report results for oxidative and thermal stability of several commercial HEFA RD samples.[11] All exhibited extremely low levels of total insoluble on the ASTM D2274 oxidation stability test and showed no evidence of thermal degradation on the ASTM D6468 thermal stability test (150°C for 180 min). However, both ASTM D2274 and D6468 were developed for diesel fuels containing 500 ppm sulfur or higher, and may not provide a clear indication of sufficient stability for ultra-low sulfur fuels such as RD.[21] CTO RD is reported to have a 32 h induction time on the EN 15751 test[18] (also known as the Rancimat induction time test), commonly used for biodiesel and biodiesel blends, a value well above the 20 h minimum required by EN 590. All available results point to the conclusion that the RD types reviewed in this guide can be handled with no additional precautions for storage and thermal stability beyond those already in place for conventional diesel. The reader is referred to the CRC Diesel Fuel Storage and Handling Guide[37] and ASTM D975 Appendix X3 "Storage and Thermal Stability of Diesel Fuels".[21]

Solubility of water

Water solubility in the nearly pure alkanes that make up RD is expected to be very low, even lower than solubility in ULSD. While water solubility is very low, the addition of additives may increase water solubility making it essential that proper handling procedures be followed per the CRC guidelines.[37]

3.3   Properties of Renewable Diesel Blends with Conventional Diesel

Lapuerta and coworkers prepared blends from a single HEFA RD and a single conventional diesel.[26] They showed that many properties blend approximately linearly – at least in the petroleum diesel that they used. These include viscosity, density, and CN. Viscosity increases for RD blending, from 2.24 cSt for the conventional diesel to 2.65 cSt for the RD. However, given the range of observed viscosity values for conventional and RD, it cannot be assumed that RD will always increase viscosity.

Because density blends approximately linearly, mass and volume based lower heating values also blend linearly.[23] For example, if RD is blended into a petroleum diesel having 5.5% higher energy content, a 20 vol% RD blend would have 1.1% lower energy content. The blend volumetric energy content reductions for blending of RD and blending of biodiesel were similar for blends below 50 vol%.[23] Density and CN results from several studies of RD blending are shown in Figure 3.2.   This figure highlights the range of density and CN that have been observed for RD (at 100 volume percent in these charts). While approximately linear blending is observed, the slope of the line varies with specific base diesel and RD being used. Additionally, the data shown in Figure 3.2 represent a very limited group of petroleum diesel and RD blendstocks, linear blending cannot be assumed for these properties necessarily.

Results for RD-diesel blend lubricity are also shown in Figure 3.2. Here the data show insignificant or only very small changes at lower blend levels, ultimately increasing above approximately 40 volume percent.

Neill and coworkers examined the response of common lubricity additives in diesel – RD blends.[38] Appropriate treat rates of ester and monoacid lubricity additives were determined for an oil sands-derived diesel fuel and were then used to treat blends of HEFA RD in the diesel fuel at the same treat rate used for the base fuel. The oil sands diesel-RD blends exhibited failing levels of lubricity on the HFRR test above 10 vol% RD for the ester additive and above 20 volume percent for the monoacid additive. Thus, the additive treat rate that was adequate for the conventional diesel was inadequate for relatively low levels of RD blending. All fuel suppliers should determine the appropriate additive treat rate for their specific diesel fuel-RD combination for the finished fuel to meet the D975 or other specification requirements.

Because of the very low aromatic content of RD, it typically increases smoke point and reduces threshold sooting index when blended into a conventional diesel with a typical 20 to 30 volume percent aromatic content.[26]
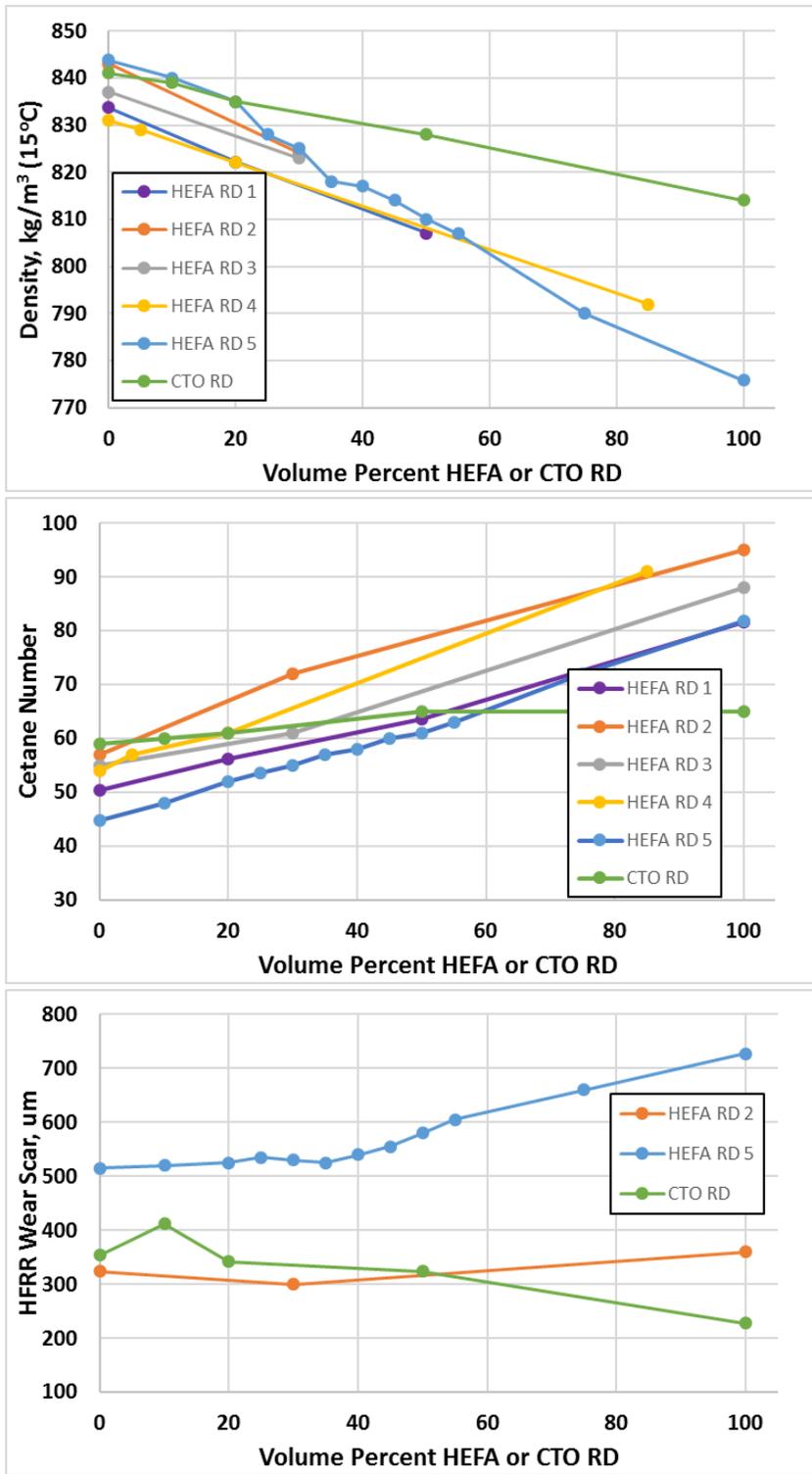
Figure 3.2. Blend density, cetane number, and lubricity for HEFA and CTO RD in several different studies. Data from references 25, 26, 29, 18, 39, 40.

Like conventional diesel, RD can be produced with a wide range of low temperature properties. Thus, it is difficult to generalize about how RD will affect low temperature operability. In many of the studies reviewed the RD exhibited a lower CP than the conventional diesel fuel used for blending leading to a lowering of CP as more RD was blended in. However, the opposite situation can occur easily.

As is also the situation for conventional diesel, CFI additive response is very specific to fuel chemistry for RD blends. Finished fuels containing RD as a blendstock would likely be more responsive to traditional CFI additives than conventional petroleum diesel fuel. Simacek et al. showed that dosages of commercial CFIs up to 800 mg/kg resulted in marginal cold filter plugging point (CFPP) improvement of a RD fuel with only 10% ≥ C_{15} n-paraffin content by weight.[41] When this RD fuel was blended at 50 wt% with an EN590 compliant fuel (excluding sulfur requirements), similar or enhanced CFI response was observed. When a less isomerized RD fuel was blended at 10 wt% into the same EN590 fuel, there was no observed response to CFI.

Similar results were observed in a study by Innospec Fuel Specialties with results reported in Figure 3.3. The CFI additive at high dosages depressed the CFPP for the fuel with 5 vol% and 10 vol% renewable diesel added. Low-temperature flow test (LTFT) results using the same blends and additive showed similar results (Figure 3.4). Blending with RD beyond 10 vol% begins to have a large impact on the effectiveness of a CFI additive. Results from Innospec also show that the n-paraffin wax distribution is shifted dramatically to higher carbon number with increased blending of RD. For example, an RD fuel was isomerized to ~20% n-paraffin content with a CP of -8°C. Blending with this RD caused a large increase of C_{16} and C_{18} waxes above the level present in the base conventional fuel (Figure 3.5).

Parties blending finished fuels are advised to work closely with their RD suppliers and, if used, CFI suppliers, to ensure the LTO properties of the RD blendstock used are fit for purpose in their geographic region(s).
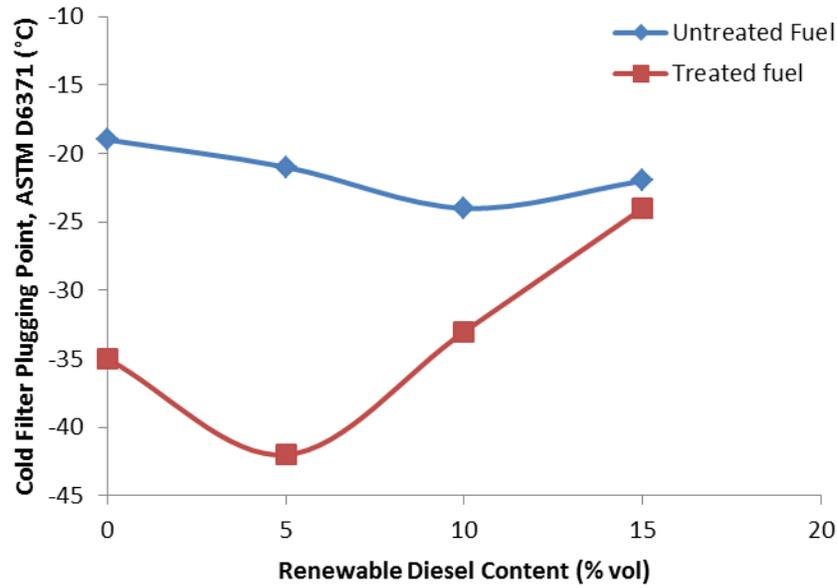
Figure 3.3: CFPP response of renewable blends treated with 500 ppm v/v active CFI.
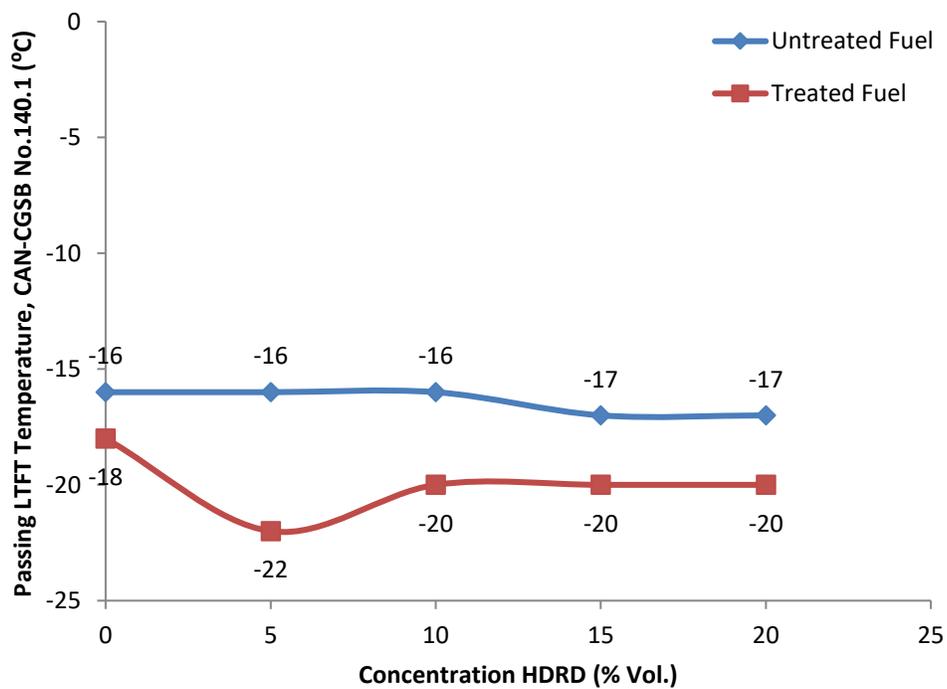

Figure 3.4: LTFT response of renewable blends treated with 500 ppm v/v active CFI.
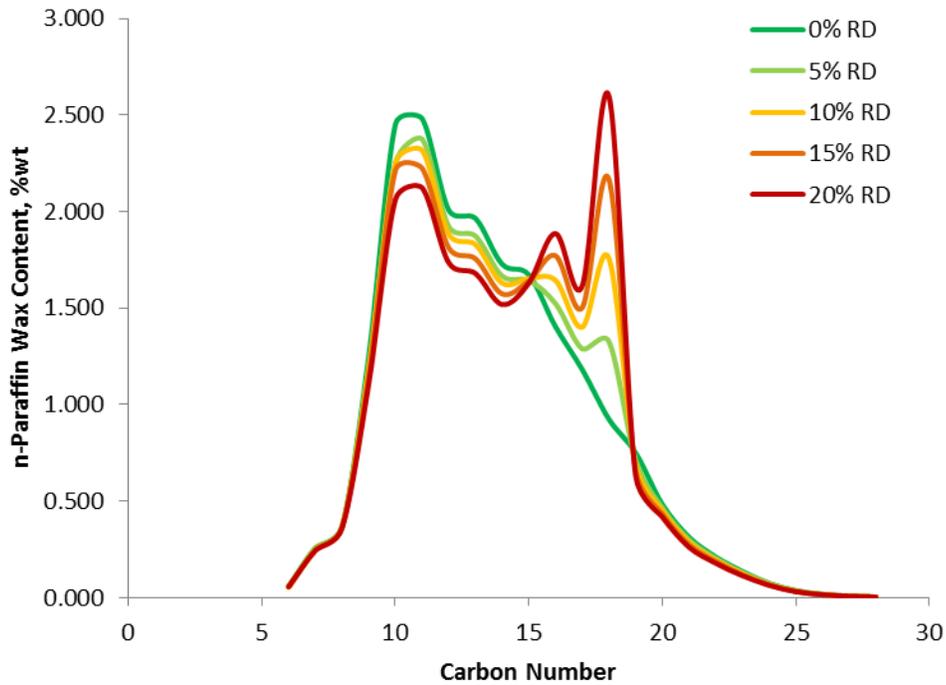
Figure 3.5: Changes in the n-Paraffin distribution with increasing RD content.

3.4   Microbial growth

Most hydrocarbon fuels such as gasoline, diesel and jet will undergo some form of degradation that forms an acetate anion and hydrocarbon fragment which is a slow process. Renewable diesel is similar to petroleum-based diesel based on physical or chemical characteristics. Therefore, users of RD either in the pure form or as a binary blend of RD and ULSD, will have the same considerations of minimizing or eliminating free water from the fuel system to guard against the likelihood or minimize the intensity of microbial contamination. As is also the case for conventional diesel fuels, those handling RD and RD blends should consult CRC Diesel Fuel Storage and Handling Guide for information on controlling water contamination.[37]

4. Fuel Distribution

4.1 Pump Labeling

In the United States, the Energy Independence and Security Act of 2007 required the Federal Trade Commission to implement a fuel dispenser labeling requirement for biomass-based diesel and biomass-based diesel blends, including RD.[42] Labels on retail fuel dispensers are required to inform consumers of the percentage biomass-based diesel present above a certain level in the fuel being dispensed. Specific labeling requirements were implemented by the Federal Trade Commission (FTC) in a rulemaking.[43] Diesel with up to 5 vol% RD does not require labeling and is treated as conventional diesel fuel. Blends containing more than 5 vol% and up to 20 vol% are labeled as containing between 5 vol% and 20 vol%, as shown on the left side of Figure 4.1. There is an option to label the top portion of this label to indicate "20% Biomass-Based Diesel Blend" or "Biomass-Based Diesel Blend," the regulations allow either of these labels to be used for any blend with greater than 5 vol% and up to 20 vol%. Blends above 20 vol% must include exact blend content (i.e. 70 vol% RD), and 100 vol% RD must also be labeled, as shown on the right in Figure 4.1. To make labeling requirements for RD identical to those for biodiesel, the FTC's current language has been confusing to many users. The following tables are an attempt to clarify the requirements from a practical point of view. Table 4.1 presents a summary of labeling requirements directly from the FTC rule. It should be noted that individual states may have labeling requirements in addition to the federal requirements.

Many users have found some of the text in the FTC tables ambiguous. Table 4.2 is our attempt to clarify the information only and is not meant as an attempt to alter the FTC requirements for wording on the labels.
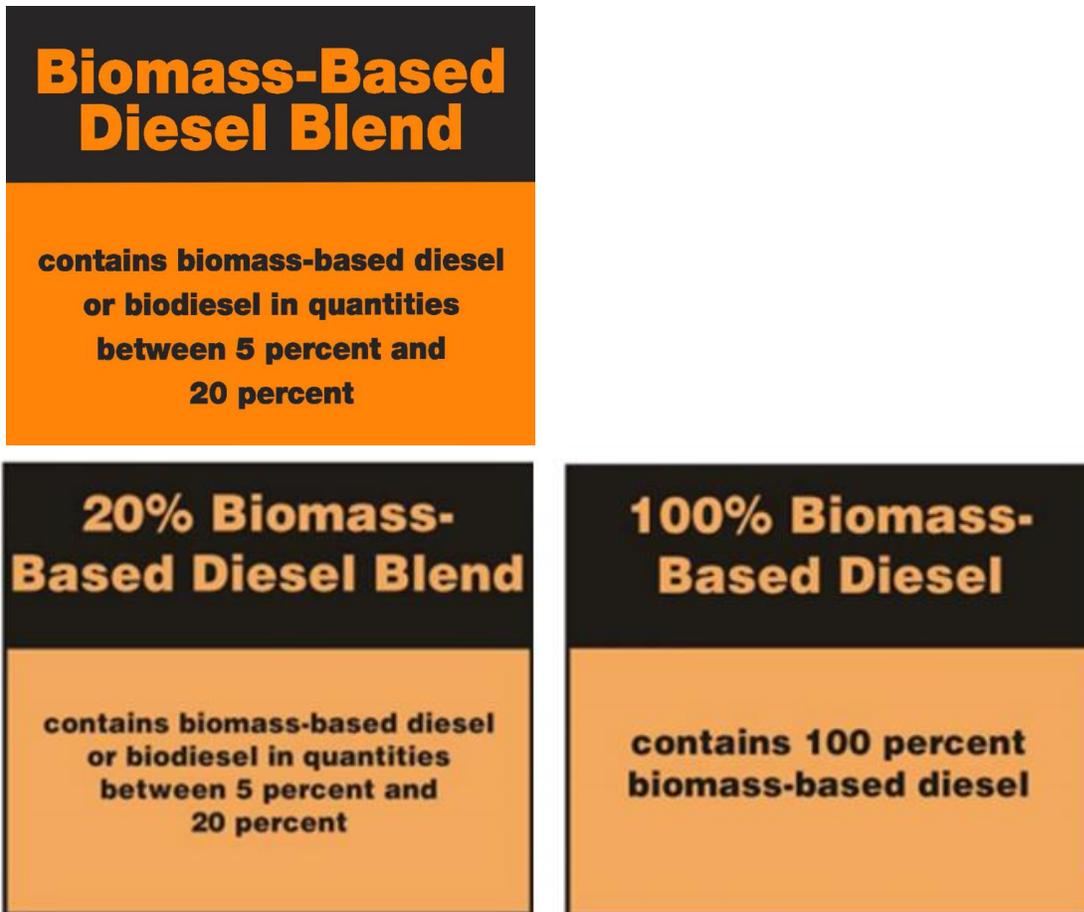
Figure 4.1. Retail dispenser labels required for renewable hydrocarbon diesel.

Table 4.1. Appendix to the FTC Fuel Rating Rule,[43] that is specific to biodiesel and biomass-based diesel labeling requirements.

(Part 1 of 2)

Fuel type	Blends of 5 percent or less	Blends of more than 5 but not more than 20 percent		
		Header	Text	Color
Biodiesel	No label required	Either "B-XX Biodiesel Blend" or "Biodiesel Blend"	contains biomass-based diesel or biodiesel in quantities between 5 percent and 20 percent	Blue
Biomass-Based Diesel	No label required	Either "XX% Biomass-Based Diesel Blend" or "Biomass-Based Diesel Blend"	contains biomass-based diesel or biodiesel in quantities between 5 percent and 20 percent	Orange

(Part 2 of 2)

Fuel type	Blends of more than 20 percent			Pure (100%) Biodiesel or Biomass-Based diesel		
	Header	Text	Color	Header	Text	Color
Biodiesel	B-XX Biodiesel Blend	contains more than 20 percent biomass-based diesel or biodiesel	Blue	B-100 Biodiesel	contains 100 percent biodiesel	Blue
Biomass-Based Diesel	XX% Biomass-Based Diesel Blend	contains more than 20 percent biomass-based diesel or biodiesel	Orange	100% Biomass-Based Diesel	contains 100 percent biomass-based diesel	Orange

Table 4.2. An attempt to clarify information in Table 4.1 only. This is not an official FTC reference document. For example, the term "Biomass-Based" used in the FTC regulation is what we have called renewable diesel in this document.

Fuel Type	Blends of 5 % or less
Biodiesel	No Label Required
~~Biomass-Based~~ Renewable Diesel	No Label Required

Fuel Type	Blends of more than 5 but not more than 20 percent		
	Header	Text	Color
Biodiesel	Either "B-XX Biodiesel" or "Biodiesel Blend"	Contains ~~biomass-based diesel or~~ biodiesel between 5 percent and 20 percent	Blue
~~Biomass-Based~~ Renewable Diesel	Either "XX% ~~Biomass-Based~~ Renewable Diesel Blend" or "~~Biomass-Based~~ Renewable Diesel Blend"	Contains ~~biomass-based~~ renewable diesel ~~or biodiesel~~ in quantities between 5 percent and 20 percent.	Orange

Fuel Type	Blends of more than 20 percent		
	Header	Text	Color
Biodiesel	B-XX Biodiesel Blend	Contains more than 20 percent ~~biomass-based diesel or~~ biodiesel	Blue
~~Biomass-Based~~ Renewable Diesel	XX% ~~Biomass-Based~~ Renewable Diesel Blend	Contains more than 20 percent ~~biomass-based~~ renewable diesel ~~or biodiesel~~	Orange

Fuel Type	~~Pure (100 %)~~ Biodiesel or ~~Biomass-Based~~ Renewable Diesel		
	Header	Text	Color
Biodiesel	B-100 Biodiesel	Contains 100 percent biodiesel	Blue
~~Biomass-Based~~ Renewable Diesel	100 % ~~Biomass-Based~~ Renewable Diesel	Contains 100 percent ~~biomass-based~~ renewable diesel	Orange

4.2   Transportation and Storage

Storage and distribution of common transportation fuels such as gasoline, jet, diesel and marine will follow a routine that has been in place for decades (Figure 4.2). After the crude oil is refined or imported refined product is received at storage tank facilities, the refined hydrocarbon makes its way through a series of bulk storage tanks, intermediate "break out" tanks, and terminal tanks from which the fuel is then transported to a customer storage tank(s) for use or sale to the consumer. The entire movement of fuel through various stages of storage is accomplished by a series of multi-product pipelines, tanker ships, barges, railcars, and tanker trucks and relies upon the fungibility of each product. In a fungible distribution system, suppliers provide volumes of interchangeable products, with offtake of similar volumes of interchangeable products but not necessarily the exact product that they provided as input to the fungible system. ULSD is an example of a fungible product. EPA underground storage tank regulations consider RD to be chemically similar to petroleum-based fuels and therefore to not require any additional notification, demonstration, or record keeping actions of owners wishing to store RD.[44]

RD (adequately treated) is fungible as far as D975 performance characteristics and properties are concerned. Depending upon the EPA registration and approved testing, RD can be used neat (with additives) or as a blendstock with ULSD. However, differences in properties of conventional diesel and RD, such as the lower density and aromaticity of RD, become difficult to detect once these products are blended. Because there is little difference in physical properties, traceability in a fungible distribution network to assure compliance with the pump labeling requirement described above can be challenging. At higher RD levels (>5%), the RD must be traced through the fungible distribution system or shipped directly to terminals where it is blended to the desired concentration before being trucked to the retail outlet.
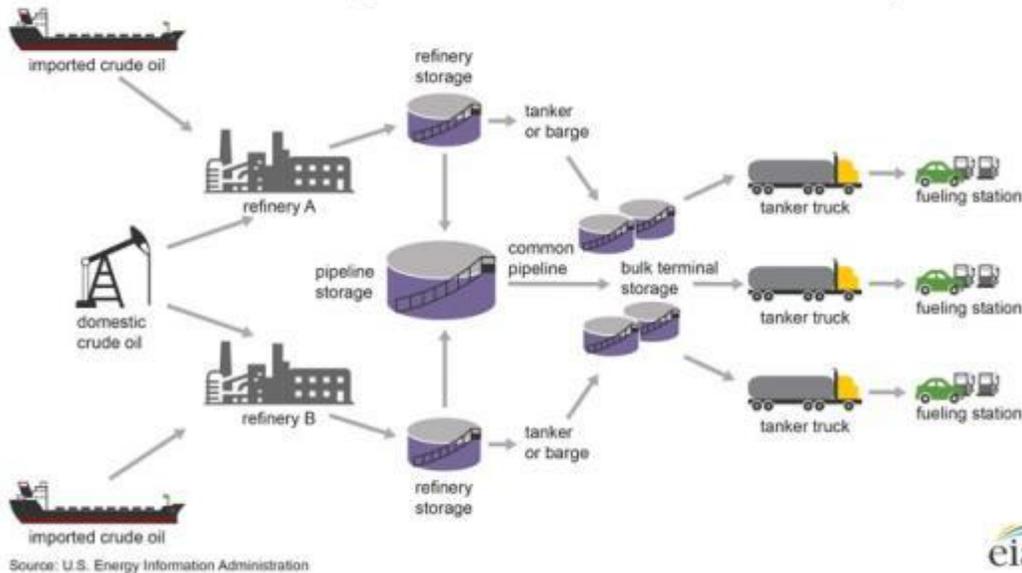

Fig. 4.2. Refined product storage and distribution.[45]

RD blend content greater than 5% can be problematic because renewable diesel consists of hydrocarbons that are chemically indistinguishable from those derived from fossil sources. The only generally accepted test method to measure renewable content is radiocarbon dating[ii] which is relatively expensive[46] and can take several weeks. [47] To reduce possible labeling violations in the United States, the industry has evolved to using no more than 5% RD in fungible blends or to direct segregated shipments of RD from producers to blending terminals where it can control the blending ratios to meet labeling requirements and add lubricity improvers and other additives as needed.

[ii] ASTM method D6866 Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis can be used for this determination.

5. Performance in Engines and Vehicles

5.1 Overview

Engine manufacturers have limited data regarding the use of RD fuels. However, several analytical evaluations have been completed to investigate what areas of concern may exist and what testing may be required to determine if those concerns are founded. Presently, most RD is HEFA that is nominally 100% paraffinic, has been isomerized to achieve required cold flow properties, additized to meet lubricity, conductivity, and other performance requirements. These fuels are characterized by properties defined by EN 15940.

New engines might be designed to take advantage of some RD properties, such as higher CN. However, when used in engines designed to operate on conventional diesel fuel, these existing engines may not benefit from these properties. Renewable diesel has a lower density and up to 5.5% lower energy content on a volume basis when compared to traditional petroleum diesel fuels. Therefore, current engines will experience a small reduction in maximum power available, a small increase in the volumetric fuel consumption, and slightly lower exhaust gas temperatures for identical duty cycles. The increase in volumetric fuel consumption will depend on the blend level and on the exact energy content of the petroleum-derived diesel and RD being blended or compared. For neat RD this could be as high as 5.5%, but for blends will scale linearly with volume percent RD because of its similarities to conventional diesel fuel.

The low aromatic content and the high CN of HEFA RD should reduce engine-out NOx emission levels enough to compensate for any reduced activity of the aftertreatment systems that results from lower exhaust gas temperatures. HC and CO emission levels are expected to be reduced when using hydrocarbon renewable diesel fuel. CTO RD should exhibit very similar emissions to conventional diesel.

Fuel system cleanliness, including internal fuel injector deposits, is not expected to be worse with RD based on experience with California and Texas low aromatic diesel fuels. Fuel solubility differences and the potential need for higher additive concentration should be considered by fuel suppliers.

5.2 Elastomer Compatibility

Elastomeric materials found in o-rings, seals, hoses, and other parts in a vehicle fuel system that contact fuel can be influenced by fuel qualities. Fuel components such as aromatics are known to cause elastomers to swell. The degree of elastomer swell is a function of both the quantity of aromatics and the sensitivity of the elastomer chemistry. Some elastomer chemistries such as nitrile rubber are more prone to swell, whereas other chemistries such as fluorocarbon, fluorosilicone, and polysulfide are less sensitive to changes in fuel aromatics content.

Lack of aromatics in neat (100%) renewable hydrocarbon diesel can affect certain elastomers adversely. The problem surfaced in the early 1990's when the US switched to lower sulfur diesel which also had lower aromatics content. The effect was amplified in California where lower aromatics diesel was also mandated. Equipment containing nitrile rubber type gaskets and o-rings developed leaks in cases where the elastomer was aged and could not handle the swelling and shrinking cycle caused by variation in fuel aromatics content.[48,49] More than 25 years of experience in elastomer selection and seal design since

this experience has resulted in improved materials selection and seal design such that most newer equipment is not expected to experience this problem.

Products with longer life cycles such as marine and locomotive engines may remain susceptible to this type of elastomer concern. A relatively simple solution for engines with these concerns is to limit the fuel used to blends that contain adequate aromatic content. A working group of the SAE International Fuels and Lubricants TC 7 Fuels Committee reached consensus that in all cases RD meeting the following conditions is acceptable for all equipment:

- Renewable diesel must be >99 vol% hydrocarbons
- Limit the amount of renewable diesel to 20 vol%
- Limit the Aromatic Content to >15 vol%
- Final fuel blend must meet ASTM D975

Operating a vehicle on a high-level renewable diesel blend or on 100% renewable diesel can similarly expose the fuel system to a significant drop in fuel aromatics and theoretically result in elastomer shrinking and fuel leaks. To date renewable diesel has been used commercially and field tested up to 100 vol% without widespread fuel leakage issues reported.[50,51] It is generally accepted that renewable diesel is compatible with the modern diesel vehicle fleet and infrastructure (CARB,[52] US DoE AFDC,[53] Natural Resources Canada[54]).

5.3   Emissions Impacts

Engine-out emissions for HEFA RD have been reported in many studies. Emission results have been summarized in reference 50 and average percent change results from that paper are presented in Figure 5.1. For light-duty the results are the average of tests for 28 passenger cars, while for heavy-duty they are the average of results for 17 vehicles. Significant reductions in engine-out particulate matter emissions are generally observed for these vehicles that were not equipped with catalysts or filters. Significant reductions in NOx (without NOx emission control catalysts) were reported for the heavy-duty vehicles, with much smaller reductions for passenger cars. Studies have also shown significant potential for even larger emission reductions in engines with optimized calibrations for the high CN and low aromatics of 100% HEFA RD.[27,55] However, these large reductions would not be obtained in current production vehicles whose engines are not optimized for RD. Research also has shown that use of 100% HEFA RD can extend the range traveled before diesel particle filter regeneration in a 2009 model year Euro 4 car.[56] For CTO RD, only small changes in NOx emissions have been observed, with more significant PM reductions for higher blend levels (on the order of 25% reduction for 100% CTO RD).[18]
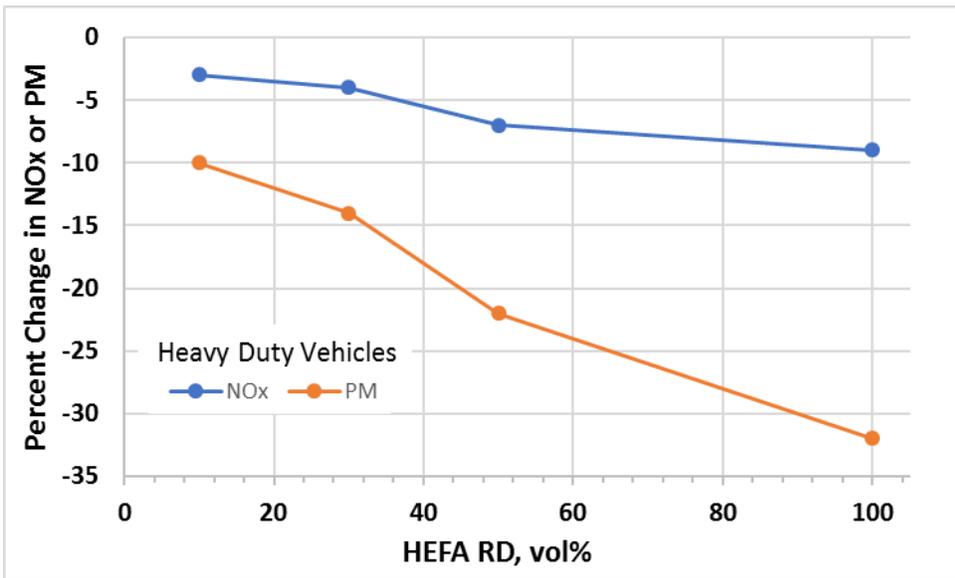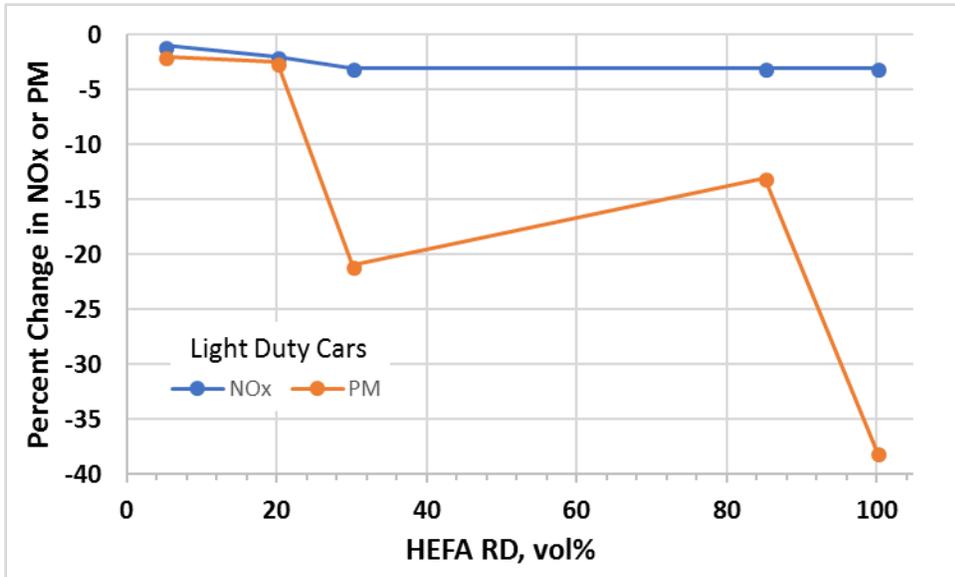
Figure 5.1. Percent change in NOx and PM engine-out emissions for various HEFA RD blend levels in both light and heavy-duty vehicles (not equipped with catalysts or filters).[50]

6. Summary

This document describes the properties of RD in neat form and in blends with conventional petroleum diesel, as well as to describe handling and blending practices, as a guide for the end user, fuel producer/distributor, and vehicle/equipment. As of 2018, RD is primarily produced by hydrotreating of esters (waste cooking oil, animal fats, and vegetable oils) or fatty acids, although there is also some commercial production from CTO. These fuels consist, primarily of normal and isoparaffins and can be produced having a range of CN and CP. Typically, lubricity and conductivity additives are required to meet minimum specifications, as is also the case for conventional ULSD. Overall, property and handling requirements for RD are similar to those for conventional USLD. RD (adequately treated) is fungible as far as D975 performance characteristics and properties are concerned. Pump labeling requirements in the United States make it difficult to transport blends containing more than 5% RD in the fungible multiproduct distribution system.

Commercially available RD is produced by catalytic hydrotreating of triglycerides and fatty acids, or hydrotreating of CTO. The hydrocarbon product from hydrogenation/deoxygenation consists of long chain alkanes that, while having a very high cetane number (CN), also exhibit a CP of over 20°C. To improve the low temperature performance of the fuel and to lower the CP, this material is hydroisomerized after removal of the water and product gases. Isomerization is likely required for RD to meet fit-for-purpose LTO properties of the finished fuel.

The properties of neat RD are generally within the ranges allowed by the ASTM D975 No. 2-D diesel fuel standard (fuel additives are necessary to meet some requirements). Notable are the very high CN and low density (relative to EN590 requirements) of HEFA-RD. Cetane number is typically above 70 for RD having CP in the range of 0°C to -30°C. Results for CTO-derived RD come from a single reference, but also show high CN. While it generally has a higher heating value per mass than conventional diesel fuels, its heating value per gallon is generally slightly lower (up to 5.5%) than that of conventional diesel. Therefore, current engines will experience a small reduction in maximum power available, a small increase in the volumetric fuel consumption, and slightly lower exhaust gas temperatures. Studies on a limited number of samples show linear blending for several properties when RD is blended with conventional diesel, including viscosity, density, CN, and lower heating value. Given the limited data, linear blending cannot be assumed for these properties.

It is difficult to generalize how RD will affect low temperature operability. As with conventional diesel, CFI additive response is very specific to fuel chemistry for RD blends. Blenders of finished fuels will need to work closely with their RD suppliers and, if used, CFI suppliers, to ensure the LTO properties of the RD blendstock used are fit for purpose in their geographic region(s).

Most newer equipment is not expected to experience any issues with elastomer compatibility. Products with longer life cycles such as marine and locomotive engines may remain susceptible to this type of elastomer concern and RD blend level may be limited by the need to retain a minimum aromatic content in the fuel.

Appendix I: Brief Overview of Future Renewable Diesel Production Routes

Co-processing adds fats and oils to the distillate stream being processed in a petroleum refinery at low levels. These products likely look very similar to conventional diesel fuels. As noted in the Introduction, GTL/FT process-derived fuels have been produced at large scale, and can, in principle, be produced from biomass-derived synthesis gas. Details of their performance and properties have been described elsewhere.[2,3]

Catalytic upgrading of sugar can take different forms, but a prominent example is Bioforming followed by condensation and hydroprocessing as proposed by Virent.[57] In the distillate fuel production incarnation of this process sugars are dehydrated over an acid catalyst, followed by aldol condensation over a base catalyst to increase molecular weight.   The products are converted to C_7 to C_{15} alkanes over a bifunctional catalyst in a complex reactor.[58] Fermentation of sugars is employed by Amyris to produce the polyunsaturated molecule fanesene (a sesquiterpene) which is subsequently hydrogenated to form farnesane, or 2, 6, 10 trimethyl dodecane.[59] This molecule was shown to have excellent diesel fuel properties with a CN of 58 and CP of -78°C. [11]   Finally, biomass fast pyrolysis produces a crude pyrolysis oil that can be hydrotreated to form hydrocarbons, some in the diesel boiling range.[60,61] While promising over the long-term, none of these processes are currently practiced at commercial scale for production of diesel.

Appendix II. Test methods for ASTM, CGSB, and CEN Diesel Specifications, and Footnotes to Table 3-1

Property	Methods		
	ISO Test Method	ASTM Test Method	CSGB Test Method
Cetane Number	EN ISO 5165* EN15195 EN16144	ASTM D613	ASTM D613* ASTM D6890 ASTM D7170
Cetane Index	EN ISO 4264	ASTM D976* ASTM D4737	ASTM D976 ASTM D4737
Density at 15°C	EN ISO 3675* EN ISO 12185	ASTM D287 ASTM D4052	
Polycyclic Aromatic Hydrocarbons*b*	EN 12916	ASTM D6591	
Aromaticity		ASTM D1319	
Sulfur Content	EN ISO 20846* EN ISO 20884* EN ISO 13032	ASTM D5453	ASTM D2622 ASTM D5453* ASTM D7039
Manganese Content	prEN 16576		
Flash Point	EN ISO 2719	ASTM D93	ASTM D93* ASTM D3828
Carbon Residue (on 10 % distillation residue)	EN ISO 10370	ASTM D524* ASTM D4530	ASTM D524 ASTM D4530*
Ash Content	EN ISO 6245	ASTM D482	ASTM D482
Water Content	EN ISO 12937	ASTM D6304	
Total Contamination	EN 12662	ASTM D5452	
Water and Sediment		ASTM D2709	ASTM D1796*c ASTM D2709
Copper Strip Corrosion Rating (3 h at 50 °C)	EN ISO 2160	ASTM D130	ASTM D130
Fatty Acid Methyl Ester (FAME) Content	EN 14078	ASTM D7371	
Oxidation Stability	EN ISO 12205 EN 15751	ASTM D2274 ASTM D7545 ASTM D5304 ASTM D6468	
Lubricity, Wear Scar Diameter at 60 °C	EN ISO 12156-1	ASTM D6079 ASTM D7688	ASTM D6079 ASTM D7688
Viscosity at 40 °C	EN ISO 3104	ASTM D445	ASTM D445

Distillation % (V/V) Recovered at 250 °C % (V/V) Recovered at 350 °C 95% (V/V) Recovered at:	EN ISO 3405* EN ISO 3924		
Distillation Temperature, 90% Recovered		ASTM D86	ASTM D86* ASTM D2887
Conductivity^d		ASTM D2624	ASTM D2624
Acid Number			ASTM D664 ASTM D974*
Low Temperature Operability	EN 116*	ASTM D2500^e ASTM D4539 ASTM D6371	ASTM D5773^{f,g}* CAN/CGSB-3.0 no. 140.1

*Indicates the referee method for the respective specification if applicable

‡Denotes specifications for EN15940:2016 Class B Paraffinic fuels

†Denotes specification values for ASTM D975 Grade No. 1-D S15 Diesel fuel

aFuels are required to have a minimum Cetane Index of 40 or a maximum Aromaticity 35% (v/v)

bFor the purposes of EN590, polycyclic aromatic hydrocarbons are defined as the total aromatic hydrocarbon content less the mono-aromatic hydrocarbon content, both determined by EN 12916

cA modified ASTM D1796 is used for the CGSB specification

dThe electrical conductivity of a diesel fuel is highly variable with temperature. For this reason, the conductivity specification must be met at the temperature of delivery. CGSB specifies that the minimum conductivity shall be met at the point of final use. ASTM D975 requires the conductivity specification to be met in all instances of high velocity transfer (defined as ≥7 m/s) with some exceptions listed in section 8.1.

eASTM D975 only provides recommendations for Low Temperature Operability (LTO) due to changes in climate across North America. Appendix X5 reviews common methods for estimating the LTO of a diesel fuel to assist in determining the desired performance of a fuel for specific applications. Compiled weather data for regions across the United States are also provided in Appendix X5 to assist in selection of LTO limits.

fCAN/CGSB-3.517 specifies that LTO properties of the fuel shall give satisfactory performance at the temperatures indicated by the 2.5% low-end design temperature data for the half month period and location of intended use. LTO properties can be determined by either the CP or LTFT. The current 2.5 percentile low end design temperature data for Canada (based upon data from 1981 to 2010 inclusive) is available at http://www.canadianfuels.ca/Fuels-and-Transportation/Conventional-Transportation-Fuels.

gMultiple methods can be used to determine CP, but ASTM D5773 is the current referee method. Other acceptable methods to determine CP for the CGSB specification are ASTM D2500, ASTM D5771, and ASTM D5772. LTFT can be determined by ASTM D4539 or by a CGSB test method.

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